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A New Monomolecular Photochemical Reaction of Allyl Radicals

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Previously unknown monomolecular photoconversion of allyl radicals, grafted onto an activated silica surface, into alkyl radicals has been found upon irradiation at wavelengths $\geqslant$370 nm and at room temperature.

Several mechanisms for the photoconversion of allyl radicals have been known for some time. According to refs. 1–3, in organic matrices at low temperature (77 K) electronically excited (340 nm $\leqslant \lambda \leqslant$ 410 nm) allyl radicals[†] abstract hydrogen atoms from neighbouring molecules resulting in matrix radicals. It has been shown[6,7] that in polyethylene upon irradiation at $\lambda \geqslant$ 390 nm and 77 K macroradicals of an allylic type convert into alkyl radicals with simultaneous destruction of the polymeric chain. Upon irradiation at $\lambda = 410$ nm in an argon matrix at 18 K allyl radicals convert into cyclopropyl radicals.[8] The same process has been observed for allyl radicals grafted onto a silica surface [$=\mathrm{Si(OH)CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$] upon irradiation at $\lambda \geqslant$ 380 nm over a temperature range 77–260 K.[9]

Thus, electronically excited allyl radicals can enter into the following reactions: i, hydrogen abstraction from matrix molecules; ii, rupture of the C–C bond at the β-position in relation to the allyl part of these radicals and iii, cyclization, when radicals of the cyclopropyl type are formed.

The aim of this work is to investigate the photochemical reactions of allyl radicals with the structure $\equiv\mathrm{Si(CH_2)_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$ without any reactive environment.[‡]

A commercially available aerosil with a surface area of 175 m^2 g^{-1} was used in this work. All of the reagents used in our experiments were commercial products used without special cleaning. The technique of photochemical activation of the silica surface was described in detail in ref. 11. Oxygen-centered ($\equiv$SiO·) centres obtained during the activation process were transformed into silicon ($\equiv$Si·) ones in the manner described in ref. 12. Allyl radicals were obtained by successive addition of ethylene (at 195 K) and buta-1,3-diene (at 300 K) to $\equiv$Si· : $\equiv\mathrm{Si}\cdot \rightarrow \equiv\mathrm{SiCH_2CH_2}\cdot \rightarrow \equiv\mathrm{Si(CH_2)_3CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2}$ (R^1). The EPR spectra of these radicals and their parameters are given in Fig. 1 and in Table 1. The EPR spectra were recorded on an X-band E-3 “Varian” spectrometer. The calculated EPR spectra were obtained by means of a home-made simulation program based on first-order perturbation theory and taking into consideration only allowed transitions. A high-pressure mercury lamp with a glassy filter, which allowed only light of wavelength $\lambda \geqslant$ 370 nm to penetrate, was used for the irradiation.

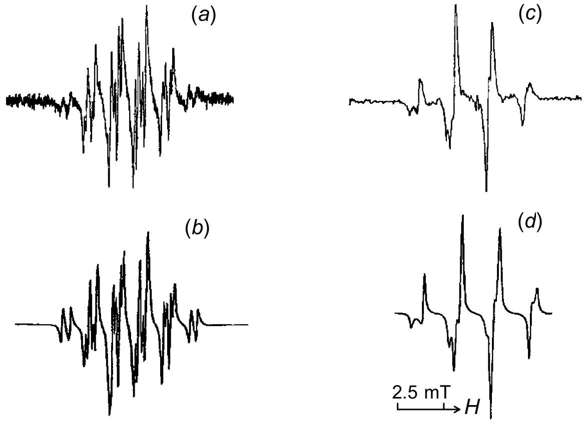
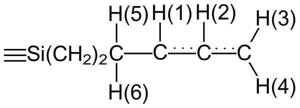
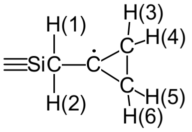


Fig. 1 Experimental (*a*, *c*) and computer simulated (*b*, *d*) EPR spectra of allyl radicals (*a*, *b*) grafted onto a silica surface and alkyl radicals (*c*, *d*) formed upon photoconversion of allyl radicals at room temperature.

[†] Maxima for UV absorption spectra of allyl radicals are *ca.* 240 and 400 nm.[4,5]

[‡] The method of matrix isolation on the activated silica surface for the investigation of photochemical reactions of organic radicals, employed in this work, was applied for the first time in ref. 10.

Table 1 EPR parameters for carbon-centered free radicals grafted onto an activated silica surface.

Radical species	$g = g_{\|\|} - g_{\perp}$	Hyperfine coupling constants/mT
$\equiv SiCH_2\dot{C}H_2$[a]	-0.0007	$a_{\|\|}^{\alpha-H} = 1.73,\ a_{\perp}^{\alpha-H} = 2.07$ $a_{\|\|}^{\beta-H} = 2.45,\ a_{\perp}^{\beta-H} = 2.55$
	0	$a_1^{iso} = a_4^{iso} = 1.25$ $a_2^{iso} = 0.38$ $a_3^{iso} = a_5^{iso} = a_6^{iso} = 1.40$
$\equiv Si\dot{C}H(CH_2)_2CH{=}CHMe$ and/or $\equiv Si\dot{C}H(CH_2)_3CH{=}CH_2$	0.0007	$a_{\|\|}^{\alpha-H} = 2.62,\ a_{\perp}^{\alpha-H} = 1.62$ $a_{\beta-H}^{iso} = 1.93$
	-0.0020	$a_1^{iso} \simeq 3.27,\ a_2^{iso} \simeq 0.20$ $a_3^{iso} = a_5^{iso} \simeq 1.88$ $a_4^{iso} = a_6^{iso} \simeq 0.70$

[a] Parameters for these radicals have been obtained earlier by Dr. Yu. V. Razskazovskii, unpublished results.

The estimation of an average distance between neighbouring radicals based on their concentration in the sample ($\simeq 10^{15}$ m^{-2}) is more than 30 nm. The estimation of an average distance between butadiene molecules based on the assumption that the whole quantity of the butadiene absorbs on the silica surface (in fact, some of the butadiene is absorbed by the glass surface of the equipment and the lubricant in the vacuum cocks of our experimental set-up) is more than 10 nm. Consequently, it may be assumed that the radicals grafted onto the silica surface have no reactive environment.

At room temperature radicals R^1 display a sufficiently symmetrical and well-resolved EPR spectrum, Fig. 1(*a*). Hyperfine coupling constants for these radicals are given in Table 1 and the corresponding calculated spectrum is shown in Fig. 1(*b*). Upon irradiation at $\lambda \geqslant 370$ nm and room temperature radicals R^1 convert into alkyl radicals with the structure $\equiv Si\dot{C}H(CH_2)_2CH{=}CHCH_3$ [or $\equiv Si\dot{C}H(CH_2)_3CH{=}CH_2$], R^2, which were identified by means of their EPR spectrum shown in Fig. 1(*c*) (*ca.* 75% of the radicals R^1 have transformed into the radicals R^2). Hyperfine coupling constants of radicals R^2 are given in Table 1 and their calculated EPR spectrum is shown in Fig. 1(*d*). The observed conversion of allyl radicals into alkyl radicals, $R^1 \rightarrow R^2$, is the same as the reaction of electronically-excited allyl radicals abstracting hydrogen atoms from matrix molecules. The only (and the most important) difference is that in our case it is a monomolecular hydrogen atom transfer process from the alkyl part to the allyl part of the excited radical. Photochemical conversion of allyl radicals into cyclopropyl radicals, mentioned in refs. 8 and 9, is not observed for radicals R^1 although we observed the same reaction for allyl radicals with the structure $\equiv SiCH_2CH{\cdots}CH{\cdots}CH_2$ under the same conditions ($\lambda \geqslant 370$ nm, 77 K) (Fig. 2). The hyperfine coupling constants obtained for cyclopropyl radicals are also given in Table 1.

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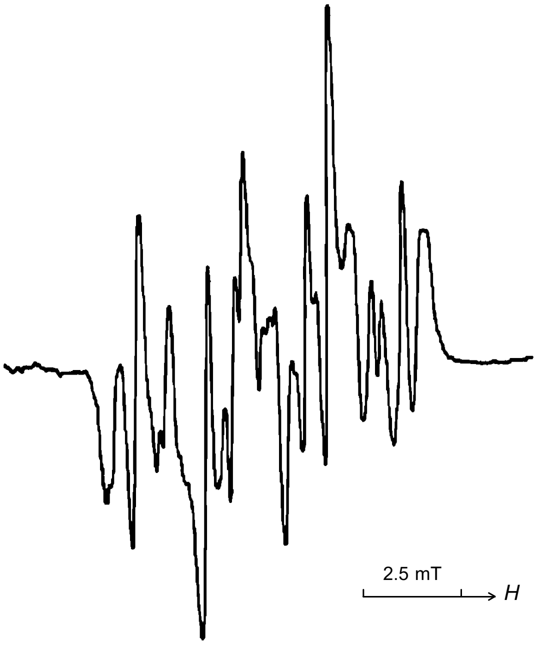

Fig. 2 EPR spectrum of cyclopropyl radicals grafted onto a silica surface and formed upon photoconversion of radicals $\equiv SiCH_2CH{\cdots}CH{\cdots}CH_2$ at 77 K.

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References

1 V. A. Roginskii and S. Ya. Pshezhetskii, *Khim. Vys. Energ.*, 1970, **4**, 240 [*High Energy Chem. (Engl. Transl.)*, 1970, **4**, 208].
2 V. A. Roginskii, *Khim. Vys. Energ.*, 1969, **3**, 473 [*High Energy Chem. (Engl. Transl.)*, 1969, **3**, 432].
3 D. R. Smith, F. Okenka and J. J. Pieroni, *Can. J. Chem.*, 1969, **45**, 833.
4 V. A. Roginskii and S. Ya. Pshezhetskii, *Khim. Vys. Energ.*, 1969, **3**, 140 [*High Energy Chem. (Engl. Transl.)*, 1969, **3**, 123].
5 V. I. Pergushov, *Vestn. Mosk. Univ., Ser 2: Khim.*, 1993, **34**, 473 (in Russian).
6 S. Simada, H. Kashiwabara and J. Sohma, *J. Polym. Sci., Part A-2*, 1970, **8**, 1291.
7 K. Tsuji, *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 467.
8 K. Holtzhauer, C. Cometta-Morini and J. E. M. Oth, *J. Phys. Org. Chem.*, 1990, **3**, 219.
9 L. Yu. Ustynyuk, V. A. Radzig and I. N. Senchenya, *Izv. Akad. Nauk, Ser. Khim.*, in press.
10 E. M. Korol'kova, V. A. Radzig and M. Ya. Mel'nikov, *Khim. Fiz.*, 1990, **9**, 1046 (in Russian).
11 N. Yu. Osokina, Yu. V. Razskazovskii, V. I. Pergushov and M. Ya. Mel'nikov, *Zh. Fiz. Khim.*, in press.
12 A. A. Bobyshev and V. A. Radzig, *Kinet. Katal.*, 1990, **31**, 925 [*Kinet. Catal. (Engl. Transl.)*, 1990, **31**, 810].

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